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Methods of Analysis of Chrome Pigments

Chemistry

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Methods of Analysis of Chrome Pigments

BY HARRY JACKSON WARNER

THESIS

FOR THE

Degree of Bachelor of Science in Chemistry

IN THE

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

H. J. Warner

ENTITLED Methods of Analysis of Chrome Pigments.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE

OF B. S. in Chemistry.

Arthur W. Palmer

HEAD OF DEPARTMENT OF Chemistry.

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In consequence of the rapidly increasing number of chrome pigments upon the market, and on account of the numerous adulterations and imitations, it is necessary to have some standard method of analysis for distinguishing of the genuine from the imitation. Some chrome pigments are comparatively simple, while in others a complete analytical analysis is necessary to determine the character. In the chrome paint industry, the sources of materials are so numerous and the number of combinations so great, that one method of analysis will suffice but for a small number of pigments. In the following investigation the object has been to determine the suitability and accuracy of the present methods upon Commercial Chrome pigments and devise any improvments to the methods that may be suggested during the work.

HISTORICAL.

It seems that the pigments used by the ancients, were for dyeing principally, and their use as paints were limited. Indigo however at that time was used as a paint, and not for dyeing. The principal pigment in Pliny's time were, white lead, cinnabar, vermillion, smalt, verdegris, red oxide of iron, and soot. Davy found cobalt in certain antique glasses, and assumes that smalt had been used in their manufacture. Native sulphide of antimony, realgar and orphiment, the sulphides of arsenic were employed extensively as cosmetics.

The Greeks protected their iron implements from the atmospheric

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encroachments by the use of metals, gold, silver and copper. So history shows that the metals of high value were the first coatings used. The ancients were not people of progress in the way of science; time was taken up with the finer arts, among which was classified the art of war. During the middle ages, Alchemy occupied the minds of the people. It remained for the scientists of the 19th Century to meet the needs of mankind, and to develope this great branch of technical chemistry. During this age of progress, the age of mammoth structures, great navies and bridges, a problem of monstrous proportions arose. How to increase the longevity of these constructions? This necessity stimulated the research on available pigments. This work has gone on until at the present day the markets of the world are flooded with pigments of varying worth.

Many are native colored earths, others are separated native metallic compounds; a large number are prepared from inorganic sources. In fact all substances colored or neutral, capable of being presented in the form of impalpable powder, which at the same time are insoluble and unalterable under ordinary atmospheric agencies may be regarded as possible pigments. A consideration of the first importance is, that the material shall possess durability and resist change of weather and other influences to which a paint is exposed.

Covering power is a very important item, especially when the paint is durable and fulfills the other requirements for any particular case. The ability of a paint to remain elastic is an important point in its favor. Paint for any place should fulfill this

requirement. In practice it may not be necessary for a paint to withstand all action, for in all probability all the unfavorable conditions will not be present. In any case the quality of the material should not be overlooked.

Pigments being so numerous and so diverse in their origin, the industry connected with the production and preparation are of necessity varied in character. Many substances employed being used in large quantities in other important industrial relations, as well as for paint, are manufactured on a large scale as for example the manufacture of white lead, prussian blue, ultramarine and chrome pigments.

CHROME PIGMENTS.

Chromium was so named on account of the many different colored compounds which it forms. Chromeum was discovered by Vaugelu in 1797. It is never found in the free state, but almost invariably as chromite or chrome iron ore $Fe\ Cr_2O_4$. This mineral is one of the products of the alteration of rocks to serpentine, and is found uniformly in association with serpentine. In America, Chromite has been found in varying quantities throughout the belt of metamorphic rocks from Maine Southward. At present the only important source of chromium is in California, where it occurs in abundance. Small quantities of the sesquooxide Cr_2O_3 are found in Chrome ochre in France and Siberia. It occurs also as the mineral Crocoite $Pocro_4$, and phoenicite $3pb0.2\ Cr_2O_3$. The color of the emerald, the verd antique marbles and the serpentines are due to the presence

of small amounts of Chromium sesquoioxide. The ores of chromum are few in number and are not very widely distributed. This element forms three series of compounds, which appear to be respectively bivalent, trivalent and sexivalent. In the chromous and chromic compounds the element acts as a base; while in the sexivalent compounds, it is of acidic character. When chromous compounds are oxidized in acid solution, the limit is reached when the chromic salt is formed. If however the action takes place in the presence of an alkali, the limit is reached by the formation of a chromate. When a chromate is treated with an acid it tends to pass back to a compound of the chromic series.

Chromium is not used in the metallic state, but is chiefly valuable for its chemical compounds, particularly the various pigments, Chrome yellow, Chrome orange, Lemon Chrome, Chrome red and Chrome green.

MANUFACTURE OF PIGMENT.

For the preparation of lead chromates, both soluble and insoluble lead salts are employed, but the best chrome yellows are only prepared from the acetate. The lead acetate is made from litharge in a lead lined hemispherical iron pan fitted with a steam pipe passing to bottom, in this is placed about $\frac{1}{2}$ amount of acetic acid necessary. The acid is heated to boiling point, and the litharge which has been ground to a cream is run in through a sieve. Steam is turned on and solution rapidly takes place. To convert this

basic salt to the neutral, the necessary amount of acid is added. Basic lead acetate has long been recognized as the best source of chrome orange, and later experiments have shown that it is admirably adapted to the manufacture of other chromes varying in shade from softest lemon to deepest scarlet.

For conversion into chromate, the basic acetate need not be dissolved in water, suspension being sufficient. Normal lead chromate Pb Cro_4 is then formed by the decomposition of the basic lead acetate by potassium bichromate. This gives a precipitate of a bright yellow color. This is rarely employed in commerce, for during the prolonged washing the color is liable to alter to a orange yellow. Yellows of similar chemical composition show very different shades, according to the amount of lead present. The larger the excess of lead the more brilliant in color is the pigment. The American"Chrome Yellow" for the production of chrome green, a pigment which owing to its peculiarity of shade is unsaleable as a yellow, but is better adapted for mixing with prussian blues than any other chrome owing to its non-liability to change.

LEMON CHROMES are usually prepared by the simultaneous action of chromates and sulphates on the lead salts, the larger the proportion of sulphate, the paler the shade of the pigment. These lemon chromes are said to be fine by the manufacturer, the lead sulphate being considered an integral part of the substance and not an adulterant. The probability is that they consist of a double compound of lead, a sulpho Chromate. The colors of the different lemon chromes can-

not be imitated by mixing together lead chromate and lead sulphate. These complex chrome yellows are much less liable to change in color than the simple chromate. Although possessing the same chemical constitution ($PbCro_4 + PbSO_4$) lemon chromes prepared by different processes possess very different shades of color and also vary considerable in physical properties, such as hardness and covering power.

	1	2	3	4	5	
Pb(C H O)3aq	400	400	400	400	400	
$K_2Cr_2O_1$	73.75	73.75	73.75	73.75	73.75	All soluble salts
H_2SO_4	49	..	..	..	..	are removed by
$A(_2(SO_4)_3$ 18aq	..	166.5	..	166.5	..	thorough washing.
NA_2SO_4	..	..	71.0	..	71.0	
Na_2CO_3	..	..	..	26.5	26.5	

In this table are given five different mixings for the production of chromes, and it will be found that the color becomes darker from one to five. The cause of the differences evidently lies in the diminishing acidity of the above formula.

CHROME ORANGE depends entirely upon the alkalinity of the liquids. By treatment of chrome yellow with caustic or carbonated alkali, they are changed into oranges, which can be made of as red a shade as desired by the employment of a sufficiently concentrated solution, the absolute amount of alkali added having no relation to the resulting color. The simplest method is to precipitate a solution of

basic lead acetate with sodium chromate, the proportion between the number of molecules of litharge and normal acetate be varied according to the shade required. If this proportion is 1 : 2, the resulting orange has the formula $Pb_2(OH)_2CrO_4$ being the most basic it is possible to prepare, therefore the deepest in color.

On increasing the litharge to its maximum 2 : 2, and having free alkali present, other compounds are formed, $1\frac{1}{2}Pb\ CrO_4\ \frac{1}{2}\ Pb(OH)_2$, which has a shade deep and fiery. The soluble lead salts may be replaced as a source of chrome yellows, by the cheaper insoluble compounds such as white lead, basic chloride and also the pure $pbso_4$. The action of the normal chromate on white lead, is to produce such bad colors as to be useless. But good results are obtained by converting a small quantity of it into the acetate. The precipitating mixture attacks the soluble portion and sets the acid free, thus the action proceeds until the white lead has all been converted into the chromate. The same process is used in the case of the basic chloride. The original chrome green was composed of the chromium oxide Cr_2O_3. It is prepared from mercurous chromate or from a mixture of ammonium Chromate and picric acid. Both processes are very expensive and for that reason it can not be used as a pigment to any advantage. This pigment is of great permanence scarcely acted upon by the strongest acids, not affected by either chlorine or sulphur gases. It is not affected by intense heat; at a white heat it melts and crystallizes on cooling. Hydrogen and carbon moxioxide do not affect it, but carbon reduced it to the metallic state on ignition. It is used principally for making green glass, porcelain and as a mordant in calico printing and dyeing.

Of all the pigments containing chromium oxide, by far the best is Guignet's green, an oxyhydrate of chromium of the formula $Cr_2O(OH)_4$. This is absolutely unaffected by light and being scarcely changed by any chemical action, is much employed for lithography and bank notes. The process of its manufacture consists in melting together at a low red heat, potassium bichromate and boric acid, the resulting chromium borate being decomposed by the action of water into the oxyhydrate.

Other pigments of this class mostly contain Chromium phosphate, the best, having regard to the cost as well as to the color, is Plessy's green. This is prepared by reducing a mixture of bichromate and mono calcium phosphate with sugar. Other pigments of considerable technical interest are the chromium silico-phospdrates and their double salts with the phosphates of the alkaline earths. Under certain conditions it is possible to prepare from them pigments with colors of unsurpassable beauty and purity. They are made by reducing with sugar a mixture of bichromate, silico phosporic acid and calcium or barium phosphate.

Green pigments are divided into two classes, (1) simple and (2) compound. The simple green pigment would be, of course, a green metallic derivative as, chromium oxide, oxychloride of copper, carbonate of copper, etc. The compound pigments are those which are composed of mixtures of blue and yellow pigments, forming different shades of green according to the proportion of each of the ingredients.

Of the commercial chrome greens, very few are chromium oxide, the great majority are usually a mixture of prussian blue and Chrome yellow. The Chrome yellow usually has the formula $PbCrO_4 + PbSO_4$. The prussian blues are of many different kinds, but generally consist essentially of fero cyanide of iron. Hydrate of alumina is generally present and also some basic salt of iron. It is frequently adulterated with calcium carbonate and starch.

ADULTERATIONS.

A large number of the Commercial pigments contain a certain amount of so called adulterant. A limited amount of adulteration does not injure the quality of a pigment, but in many cases improves it, as often great disadvantages are connected with the use of the pure pigment which is alleviated by the use of some inert material mixed with the pure pigment. Adulteration of pigments are of two kinds, organic and inorganic. Organic adulteration is certainly injurious to a pigment, as in most cases the organic material is either wholly or partly soluble in water, and so as a paint would be of little use. Organic pigments are readily detected as most of them are easily soluble in water or alcohol. The inorganic substances most used for adulteration purposes are barytes, Raolin, ground silica, ground gypsum, whiting, China Chay, Talc, and ground feldspar.

Barytes is often used in pigments that are sold by weight, on account of its high sp. gravity, there being no other special advantage in its use. To a certain extent it can not be said to be injurious, as it is one of the most durable of materials and possess-

es considerable covering power.

Silica is not injurious to a pigment if it is in a fine state of division, but on account of its hardness is rarely ground fine enough to be of use.

Talc and Kaolin have nearly the same physical characteristics as a pigment, do not grind well, and when mixed with a paint do not adhere to a surface.

Feldspar should never be used as a pigment when the paint is to be applied out doors, for it readily decomposes under atmospheric agencies.

Whiting is used to quite an extent in the manufacture of white pigments. The only danger seems to be that the oil may react with the whiting and form a kind of soap.

Gypsum, on account of its great durability, chemical inactivity low specific gravity, and cheapness presents the most advantages and the least disadvantages of any substance used as a pigment adulterant.

The question is often asked, how much inert material can be used in a pigment, without injuring its properties. Each pigment is able to bear a certain amount of inert material, this amount varying according to the nature of the pigment. One pigment examined, contained four parts of inert material to one pigment. The general rule observed is that as much inert material may be used as will give good optical covering power, when the paint is properly mixed and applied. Necessarily this amount depends on the finess of the grinding, the finer the paint is ground, the more inert material

can be used without interfering with the covering power. In all cases there should be no possibility of a chemical reaction between the adulteration and the main pigment. Chrome green, made by mixing chrome yellow and prussian blue, fades very readily. It has not been decided whether a reaction takes place between the adulteration and the pigment, orbetween the pigments themselves. Most of the pigments sold under the name of Chrome green, Chrome yellows and Chrome reds hold a large amount of inert material, such as barytes, silica, etc. It is necessary therefore to have a rapid and accurate method for the detection and analysis of such mixtures.

The first essential in the analysis of a pigment, is the getting it into solution as completely as possible. It was found that Con H Cl would dissolve the lead chromate, most of the lead sulphate, a trace of prussian blue, leaving $BaSO_4$, $Pb\ SO_4$, SiO_2 and most of the prussian blue undissolved. Nitric acid and dil sulphuric acid only dissolved a portion of the pigment. Con sulphuric acid dissolved the pigment entirely, but upon dilution of the solution with water or alcohol, the iron, lead and barium were immediately thrown down. It was found that a solution of Nas H converted prussian blue, on heating into ferric hydroxide, which dissolves in H cl. Lead chromate on similar treatment is changed into the basic lead chromate, also easily soluble in Hcl. $Pbso_4$ on long treatment with Nao H dissolves completely. $2Pbco_3 + Pb(o\ h)_2$ dissolves partially in Nao H, and the remainder goes into solution readily, when excess of acid is added.

Thus by the action of an bceoH solution on a pigment, which is composed of all or part of the following ingredients, $Pbso_4$, $Baso_4$, $2Pbco_3 + Pb(o\ H)_2$, PbCr O_4, $K_2Fe_2(FeCN)_2$, and subsequent addition of an excess of Hcl everything goes into solution except $Baso_4$. A strong enough solution must be used, about 18 grains of Nao H to 100 c.c. of distilled water, and the pigment must be heated with it for at least $\frac{1}{2}$ hr., or the prussian blue and lead sulphate will not be completely decomposed..

METHODS OF ANALYSIS.

Preparation of sample for analysis.

(1) Grinding and passing through 100 mesh sieve and mixing.
(2) Qualitative examination.
(3) Ultimate quantitative analysis showing elements present.
(4) Proximate quantitative analysis showing the forms in which these elements are combined.

Method (1) Acid solution.

To 1 gr. sample of chrome green, add 25 c.c. Hcl and heat to boiling several minutes, add water, allow to stand 10 minutes and then filter. Wash residue thoroughly with hot water.

Residue.- Prussian blue and Ba SO_4 or other insoluble matter. Dry and ignite.

Filtrate.- Nearly neutralize with NH_4OH leaving however the solution slightly acid. Pass H_2S through solution until lead is all precipitated. Allow to settle, filter and wash. Dissolve PbS with hot Hno_3(14) and boil. Filter from sulphur and bring filtrate to small bulk by evaporation with several additions of H_2SO_4. Evaporate to

fumes of H_2SO_4, cool and add water and alcohol, filter, wash, ignite and weigh as $Pbso_4$ as usual.

Filtrate. Cr(and Fe) boil off H_2S, add NH_4o H in slight excess, boil this off and wash the $Cr(o\ H)_3$ and $Fre(O\ H)_3$ as customary. After weight is obtained mix with 1 part Kno_3 and 3 parts of Na_2Co_3 and fuse in platinum crucible to clear fusion, boil with water, filter, and wash.

Filtrate for Cr. Precipitate with NH_4OH in glazed porcelain dish as usual. If not of Cr_2O_3 is very nearly same as before, there has been no iron extracted from the Prussian blue in the acid treatment. Some varieties are affected, others are not. If the wt. is less than original, deduct it from same, the result is Fe_2O_3, which is also to be calculated to Prussian blue and added to other.

Residue.- Filter, wash, dry and ignite, weigh as Fe_2O_3, if wanted as a check.

Det. SO_3.- 1 grain is heated with 25 c.c. con Hcl, filtered from Prussian Blue, and SO_3 in filtrate determined as $BaSo_4$.

Chrome yellow, Lemon Chrome, and Orange Chrome:- The method is slightly varied for these pigments. To 1 grain of pigment, 25 c.c. con Hcl is added and heated. Any insoluble matter, such as barytes or selica, to be filtered out, washed, ignited and weighed. Further its weight is to be deducted from that of the total lead weighed as sulphate.

Lead.- 1 grain treated in a covered casserole with 25 con H_2SO_4 and heated moderately until residue is perfectly white, cool, dilute with 50 c.c. water, heat and again cool, add 50 to 75 c.c. of 94%

alcohol, stir and allow to stand for 1 hr. Filter, wash with alcohol dry, ignite ½ hr, treat with HNO_3 + H_3SO_4, heat again 15 minutes, cool and weigh.

Chromium and Sulphuric acid (SO_3).

Treat 1 grain with about 25 c.c. con Hcl., boil, dilute to 100 c.c. and while hot, add excess NH_4OH, which precipitates the Chromium and greater part of lead. Boil off excess of NH_3, filter, and wash very carefully with hot water.

Precipitate for Cr.: Dissolve in dil. Hcl. neutralize excess of acid with NH_4O H, precipitate lead with H_2S and filter into porcelain dish. Precipitate rejected. Boil off excess of H_2S from filtrate and precipitate Cr. with NH_4OH in usual manner. Put moist precipitate into crucible and ignite carefully. Weigh as Cr_2O_3.

Filtrate for SO_3.: Acidify with Hcl. and concentrate. Add boiling $Bacl_2$, drop by drop and determine SO_3 in usual manner, taking care to wash precipitate very thoroughly with hot water.

Occasionally the following determinations are made:

Hydroscopic Water:- Heat ½ grain at 220° F. in an air bath to constant weight. Loss.

Volatile Matter:- Heat 1 grain in porcelain crucible to gentle redness. Loss minus hydroscopic water is volatile matter.

Water Extract:- Acetates, sulphates, bichromates or nitrates of soluble salts medicating imperfect washing. Treat 3 grains with successive portions of 20 c.c. each cold distilled water, decanting and filtering each time. Evaporate filtrate in platinum dish to dryness over a water bath.

METHOD 2.- Alkaline solution chrome green. A 1 grain sample was weighed out into a beaker, 100 c.c. NooH(18 grains to 100 c.c.) was added and beaker covered with walch glass, and heated for $\frac{1}{2}$,hr., until all of the prussian blue was decomposed. Allowed to cool, until acid could be added safely, then 50 c.c. con *HCl* was added and whole heated for 15 minutes.

Residue for $BaSO_4$: There is obtained by this process a greenish yellow solution and a pure white residue. The solution was now filtered, and residue washed thoroughly with hot water. The residue should now contain nothing but $BaSO_4$ and SiO_2 . The precipitate is now transferred to a platinum crucible and ignited and weighed. This gives the weight of the $BaSO_4$ and $Si\ O_2$. The SiO_2 if present was then volatilized by means of hydro fluoric acid. Residue, dried ignited and weighed again. Loss in weight is SiO_2 .

Ammonium tartrate solution is sometimes used to wash the $baso_4$ residue on the filter, inorder to completely extract the $PbSO_4$. This was not found necessary however, if the pigment was heated long enough with the NaoH solution.

Filtrate from $BaSO_4$: NH_4oH was now added until the solution was only slightly acid, and the lead was precipitated by passing H_2S through it. The solution was then filtered and precipitate washed with water. Filtrate and washings were set aside for determination of Cr, Fe, So_3 .

The precipitate (Pbs): was then dissolved in con $H\ N\ O_3$ and heated care being taken that all $Pbso_4$ found is held in solution. The solution was then filtered to take out sulphur, and 25 c.c. con H_2

SO_4 was added to the solution in a porcelain casserole, and the whole evaporated until fumes of SO_3 were given off, cooled, diluted with 50 c.c. of 94% alcohol, allowed to stand a couple of hours and then filtered. The precipitate was well washed with 94% alcohol, dried, ignited and weighed as $pbso_4$. All lead in pigment obtained as $bobso_4$.

Filtrate from PbS: The filtrate from PbS was heated until H_2S was all driven off, made alkaline with NH_4OH, excess boiled off. $Cr(OH)_3$ and $Fe(OH)_3$ are filtered out, washed thoroughly with hot water, dried, ignited and weighed. Cr and Fe separated and determined as in Method I.

So3d0t. : Filtrate from $Fe(OH)_3$ and $Cr(OH)_3$ acidified and SO_3 precipitated as $BaSo_4$ and determined as usual.

METHOD (3) . This method is only an improvement on method (2) in accuracy and quickness of determination. It was found by experiment that the last substance to dissolve under the influence of Nao H, is the lead white. This substance dissolves much more readily in con Hcl, than in Nao H, so by applying con Hcl directly to residue left from Nao H sol. the lead white is quickly dissolved out, and also any traces of $PbSo_4$ or $PbCro_4$ that may remain.

Solution: 1 grain of chrome green was treated with 100 c.c. NaoH (18 grains) in a covered beaker, and heated for 20 minutes, cooled, diluted with water. 50 c.c. con Hcl, the necessary amount to produce acidity was measured out. 25 c.c. con Hcl was added to reduce the alkalinity, so that it could be safely filtered. The solution was decanted on to the filter, the residue in beaker was washed

with hot water and decanted again, the remaining 25 c.c. con Hcl was added to residue in beaker and heated for 10 minutes. This acid solution was filtered through the same filter as the NaoH solution and into the NaoH filtrate. In this way, a perfectly pure white residue was obtained, which contained no trace of lead or prussian blue. The slightly acid filtrate contained all the iron, chromium and lead in solution.

Residue: The residue left on the filter was washed thoroughly with hot water, dried, ignited and weighed. If Sio_2 was shown to be present in the qualitative examination, then it was volatilized from the crucible by use of hydrofluoric acid, the crucible and contents being weighed again, the loss calculated to $Si\ O_2$.

Filtrate: NH_4oH was added to the solution until it was only slightly acid. Lead was precipitated by H_2S allowed to settle and then filtered out. Determined lead as in Method I.

Chromium, Iron and So_3: Solution heated until H_2S had passed off, filtered from sulphur, into a 250 c.c. flask graduated and made up to mark with distilled water.

The chromium and iron were determined by means of a volumetric method employed in the analysis of Chrome iron ore. 50 c.c. was drawn from the flask and placed in a beaker and heated to boiling. Crystals of $Kmno_4$ broke up, and mno_2 separated. The mno_2 was filtered from the solution. All of the chromium had been oxidized to $H_2Cr\ O_4$. To the solution, 20 c.c. $Feso_4$ of a known iron value was added, the $FeSO_4$ reduced the H_2Cro_4 and the excess of $Feso_4$ was titrated with standarized $Kmno_4$. Thus, knowing the value of both

$FeSO_4$ and $Kmno_4$, it can be determined how much $FeSO_4$ was necessary to reduce the H_2CrO_4. Therefore from the equation,

$6\ FeSO_4 + 2\ Cro_3 + 6\ H_2SO_4 = 3\ Fe(SO_4)_3 + Cr_2(SO_4)_3 + 6\ H_2O$ it can be determined how much Cr_2O_3 each c.c. of $FeSO_4$ is equivalent to, and from this data can be calculated the amount of Chromium in the pigment, and also the amount of $PbCro_4$.

In the iron determination, 50 c.c. was placed in an Erlenmeyer flask diluted with water, zinc and a little Hcl added to reduce iron to ferrous state, a stopper with glass tube and rubber joint containing a slit for escape of hydrogen, was placed in flask. The whole was now heated until zinc had nearly all disappeared, Na_2HPO_4 was then added to take up excess of Hcl. The solution was filtered through glass wool, cooled quickly and titrated with standarized $KMno_4$. From the amount of iron found, the prussian blue was calculated. In some prussian blues some aluminum is contained as alum. 50 c.c. of solution taken, and Fe Cr al precipitated by means of $NH_4O\ H$, filtered, washed, dried, ignited and weighed. Thus the total weight less that of iron and chromium found volumetrically will give the weight of the aluminum.

So_3 determination. For this determination, 100 c.c. was taken, heated to boiling and So_3 precipitated by $Bacl_2$. Weighing as $Baso_4$. From amount of So_3 the $Pbso_4$ was calculated. The remainder of the lead which was not calculated to $Pbcro_4$ and $Pbso_4$ was calculated to lead white $2\ PbCo_3 + Pb(OH)_2$.

Commercial Chromes.

The three methods of analysis for Chrome paints given in the preceding pages were tried carefully upon a number of commercial chrome paints, in order to test ~~accuracy~~ accuracy and speed of method. The analytical results are given in the following tables.

Chrome Green

Constituents.	Method I	Method 2	Method 3.
	Average of 3 analyses.	Average of 3 analyses.	Average of 3 analyses.
Isol Res. $BaSO_4$,	67.76%	63.72%	58.50%
$PbCro_4$	15.06%	15.14%	15.43%
$PbSo_4$	6.56%	4.75%	6.52%
$2PbCo_3+Pb(OH)_2$	1.16%	.61%	1.09%
$K_2Fe_2(FeCN)_2$	Remain in Insol Res.	18.40%	18.87%
Total	----------	102.62	100.41%

By the acid treatment in method I, the prussian blue could not be dissolved entirely. About $\frac{1}{2}$ of the prussian blue was insoluble and so was left on filter with the barum sulphate, and on ignition became Fe_2O_3 . The prussian blue that dissolved was partially reprecipitated as soon as the acid solution was diluted and cooled. And thus the reprecipitated prussian blue was collected on the filter with the Pbs and left there after the Pbs had been dissolved in HNO_3.

Method 2 gave better results, in that a complete extraction of prussian blue was obtained. The unsatisfactory thing about this method was the difficulty in getting all of the $Pbso_4$ and $2PbCo_3 + Pb(OH)_2$ in the alkaline solution. Ammonium tartrate would dissolve out the lead salt, by continued treatment but this took a great deal of time, and the two filtrates had to be kept separate, so the method proved very tedious and did not give as good results as desired.

Method 3. gave results that were very satisfactory. By the use of alkali and acid as solvents, all the iron, chromium and lead was obtained in solution, the barum sulphate being left on the filter in a pure condition. Method 3 besides being much more accurate was also a great deal speedier than method 2.

Chrome orange was next analyzed, Methods 1 and 2 being used.

Chrome Orange.

Constituents.	METHOD I. ACID. Results Average of 3 analyses.	METHOD 2. ALKALINE. Results Average of 3 analyses.
$BaSO_4$	56.46%	58.53%
$PbCro_4$	25.19%	24.79%
$Pbso_4$	3.08%	2,12%
$2\ PbCo_3 + Pb(OH)_2$	13.87%	13.08%
Moisture	.31%	.31%
Total	98.91%	98.83%

In this pigment, the acid method of solution works the best as will be seen by the results obtained. As there is no prussian blue in this pigment, that difficulty is eliminated, the ~~xxxxxxxxxx~~ ~~xxx~~ ingredients, with the exception of $BaSO_4$ dissolve in acid. The alkaline method of solution fails as in the chrome green, to completely dissolve out $Pbso_4$ and $2PbCo_3 + Pb(OH)_2$. Thus the results will be low in lead sulphate and white lead, and correspondingly high in the $BaSO_4$ residue.

Lemon Chrome was the next pigment to be analyzed.

LEMON CHROME.

Constituents.	Method. Acid. Average of 3 analyses.	Method. Alkaline. Average of 3 analyses.
$BaSO_4$	80.28%	80.48%
$PbSO_4$	4.57%	4.24%
$PbCro_4$	15.09%	15.05%
Total.	99.94%	99.77%

The results obtained by both methods were good and agreed well, but the acid method is to be preferred as it proved to be speedier

PIGMENTS OF KNOWN PROPORTIONS.

In order to more fully test the accuracy of method 3, pigments of known per cent. ingredients were made up, and analyzed. The

materials used were, $BaSO_4$, $PbSO_4$, $PbCrO_4$, $K_2Fe_2(FeCN)_2$, $2PbCO_3$ + $Pb(OH)_2$, and Cr_2O_3. The C.P. materials were taken and tested as to purity; many samples were not pure, and required a great deal of washing to remove soluble salts. The $BaSO_4$ was made by dissolving $BaCO_3$ in Hcl, precipitating with H_2SO_4 and washing until filtrate showed no acid. Cr_2O_3 was prepared in pure form, by precipitating a solution of potassium chromate with Hg $N.O_3$ washing thoroughly, and igniting until mercury was driven off and Cr_2O_3 remained in the crucible. Each salt was purified until it was shown to be pure by analysis. Each salt was ground, passed through a 100 mesh sieve and well mixed. A pigment was then made up, known quantities being weighed out. The different ingredients were well mixed, first by grinding and then passing through a 100 mesh sieve several times, until the pigment became uniform in color. Each pigment thus made up, was analyzed three times by method 3 in order to test accuracy of method.

The following analytical results were obtained.

Ingredients.	Known % by Weight.	Results obtained by METHOD 3.
$BaSO_4$	50%	49.92%
$PbCrO_4$	40%	39.88%
$PbSO_4$	2.5%	2.56%
$2PbCO_3+Pb(OH)_2$	2.5%	2.48%
$K_2Fe_2(FeCN)_2$	5%	4.91%
	100%	99.75%

In pigment No. 1, the object was to make up a pigment, as near like the commercial chrome green analyzed as possible. No difficulty was experienced in the application of the method to pigment 1 and good results were obtained.

PIGMENT 2.

Ingredients.	Known % by Weight.	Results obtained by METHOD 3.
$Baso_4$	60%	59.87%
$PbCro_4$	35%	34.96%
$K_2Fe(FeCN)_2$	5%	5,01%
Total	100%	99.84%

Pigment 2 was made up with the object of determining what effect $Pbso_4$ and $2PbCO_3+Pb(OH)_2$ had on the analysis of a chrome green. All the other pigments hitherto analyzed had contained these ingredients, but in pigment 2 they were not used. However the only noticeable effect was in the decomposition, a shorter time being necessary than in the others.

PIGMENT 3.

In-gredients.	Known % by Weight.	Results obtained by METHOD I.	Results obtained by METHOD 3.
$PbCrO_4$	75%	74.89%	74.92%
$K_2Fe(FeCN)_2$	15%	13.96%	14.95%
$PbSO_4$	5%	4,98%	4.96%
$PbCO_3+2Pb(OH)_2$	5%	5.02%	4.93%
		98.85%	99.76%

The object in making up pigment 3 was to determine the effect of the adulterant Baso4 upon the method 3. $Baso_4$ was not used in making this pigment, so, in the only possible case that method 1 could be of any use, it was tried to compare it with method 3. Method I (acid solution) is supposed to leave the prussian blue, undissolved, and so two determinations had to be made. Then by comparison of results it will be seen that much better results were obtained by method 3. By method 1, it is difficult to obtain an accurate determination of the prussian blue. Some of the prussian blue passes through the filter and remains suspended in the solution in a finely divided state, thus when the lead is precipitated and filtered, some of it is left on the filter, and lost.

PIGMENT 4.

Though Cr_2O_3 is seldom found in a pigment on account of its

cost, it was thought well to try Method 3 upon it, in order to prove the worth of the method in all chrome greens. It was found however that Cr_2O_3 would not dissolve without difficulty in a concentrated solution of Nao H. But the difficulty was overcome by fusing with Nao H and then dissolving in water and acidifying. In this way an accurate analysis of chromic oxide can be obtained.

RESULT OF INVESTIGATION.

(1) That method I (acid solution) is entirely worthless in the analysis of a Chrome Green.

(2) That method (2) (alkaline solution) is defective in Chrome pigment analysis and can not be relied upon to give accurate results.

(3) Method 3. Treat pigment with a solution of Nao H, filter, treat residue with Con Hcl filter. Two filtrates are mixed, lead removed as PbS and determined as $PbSO_4$. Chromium and iron determined by volumetric methods, So_3 determined as $Baso_4$. This method proved to be accurate and speedy upon all chrome greens, that it was tried on. By the method all the pigment goes into solution with the exception of $Baso_4$ or Sio_2. Clean filtering and complete separations are characteristic of the method. On account of the volumetric method used for iron and chromium, the analysis is quickly and easily performed.

This method ought to prove applicable to all Chrome pigments, of course modifications will be necessary according to the varying constituents of each pigment.

LIST OF REFERENCES. FACTORS.

The following table of factors were calculated and used during the work upon this thesis.

Ba=137. C=12. Cr=522. Fe=56. H=1. K = 39. N = 14. O = 16. Pb = 207. S = 32.

FOUND.		SOUGHT.		FACTORS.
$BaSO_4$	(233)	$Pbso_4$	(303)	1.300
$BaSO_4$	(233)	Pb.	(207)	.888
Cr_2O_3	(152.4)	$2Pb\ Cro_4$	(646.4)	4.241
Cr_2O_3	(152.4)	2Pb.	(414)	2,716
Fe_2O_3	(160)	$K_2Fe_2(FeCN)_2$	(354)	1.106
Pb.	(207)	Pbo.	(233)	1.077
Pb.	(207)	$Pb\ Cro_4$	(3232)	1.561
3Pb.	(621)	$2Pbco_3+Pb(OH)_2$	(775)	1.248
$PbCro_4$	(323.2)	Pb.	(207)	.640
$Pbso_4$	(303)	Pb.	(207)	.613
SO_3	(80)	$Pbso_4$	(303)	3.7875

References.

(1) Fresenius Quantitative Analysis.

(2) Select Methods. Crooke.

(3) Carins Quantitative Analysis.

(4) The Chemical analysis of Iron. Blair.

(5) Fresenius Qualitative Analysis.

(6) Allen's Commercial Analysis.

(7) Prescott's Quantitative Analysis.

(8) Sutton's Volumetric Analysis.

(9) Dictionary of Solubilities.

(10) Paint Analysis. Walter Lee Brown.

(11) Chemical Journals.

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